Investigation on the Effect of GO Membrane Modification and Intercalation Regulation on Solute-Selective Separation

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Abstract: Graphene oxide (GO) membranes have attracted significant attention in water treatment and ion separation due to their tunable two-dimensional nanochannels. However, in practical applications, GO membranes often suffer from a trade-off between permeability and selectivity, which is strongly influenced by interlayer spacing and surface functional groups. Therefore, regulating the interlayer channels and chemistry is essential for improving their separation performance. In this study, GO membranes were modified by carboxylation and intercalation to investigate the relationship between membrane structure and separation performance. Firstly, the loading of GO and carboxylated graphene oxide (CGO) was optimized, and the optimal loading was determined to be 31 $mg \cdot m^{-2}$. CGO membranes exhibited better hydrophilicity and higher water flux due to the introduction of carboxyl groups. Subsequently, Ca^{2+} and ethylenediamine (EDA) were introduced for intercalation modification. Separation performance results demonstrated that an appropriate Ca^{2+} intercalation ratio significantly improved the rejection of NaCl, $MgSO_4$, and PEG-600, while excessive addition reduced performance. In contrast, EDA intercalation decreased rejection but increased water permeability. In addition, all membranes exhibited higher rejection for $MgSO_4$ than NaCl, indicating a charge-based separation effect..

***Keywords*:** Graphene oxide;Carboxylation; Intercalation regulation; Selective separation

1. Research Background and Significance

With the continuous development of society, economy, and industrial production, water resource shortage and water environmental pollution have drawn increasing attention. Efficient, energy-saving, and stable water treatment technologies have become a key research priority. Membrane separation technology, characterized by simple operation, small footprint, no phase change, low energy consumption, and stable separation performance, has been widely applied in drinking water purification, industrial wastewater treatment, ion separation, resource recovery, and other fields [1]. Among various membrane materials, graphene oxide (GO) membranes, with their unique two-dimensional lamellar structure, tunable interlayer channel size, and abundant oxygen-containing functional groups on the surface, exhibit good hydrophilicity and demonstrate significant advantages in ion sieving, small molecule separation, desalination, and heavy metal removal, making them an important focus of novel separation membrane research[2].

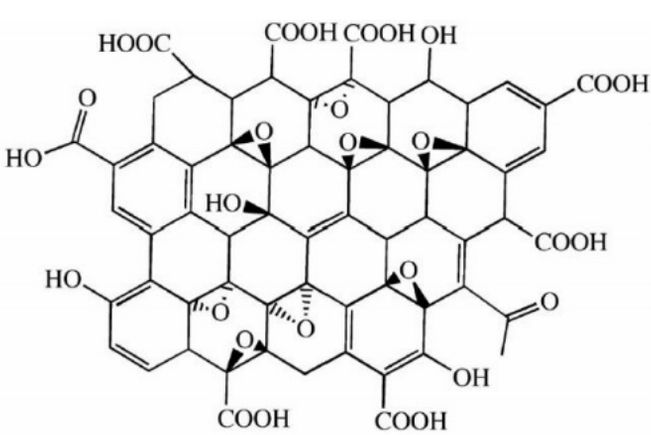

Figure 1. Molecular structure of graphene oxide[3]

However, pure GO membranes still suffer from many deficiencies in practical applications. The membranes tend to swell in aqueous solutions, leading to enlarged interlayer spacing, reduced structural stability, and significantly decreased ion selectivity. Meanwhile, it is difficult to simultaneously improve water flux and rejection rate, and the performance tends to

decay during long-term operation. Moreover, acid/alkali resistance and anti-fouling ability also need further enhancement[4]. These issues restrict the application of GO membranes in high-precision separation and complex water treatment scenarios.

To address these issues, researchers have commonly employed modification, cross-linking, intercalation, or compositing methods to optimize the structure of GO membranes, stabilize the lamellar structure, precisely regulate interlayer spacing, and adjust surface charge and hydrophilicity/hydrophobicity, thereby improving membrane stability and separation performance[5]. By introducing polymeric materials or metal ions, stable linkages can be formed between nanosheets, suppressing membrane swelling, optimizing ion transport channels, and enhancing the selective separation capability for different solutes. Therefore, conducting research on the modification and intercalation regulation of GO membranes holds significant theoretical value and practical significance for developing high-performance, high-stability water treatment membrane materials[6].

2. Experimental Methods

2.1 Modification of the Support Membrane

First, weigh 0.5 g of dopamine hydrochloride powder and add it to an appropriate amount of tris-HCl buffer solution; stir until completely dissolved to obtain a PDA solution. Then, immerse the PVDF support membrane in the PDA solution for 3 h, place it in an oven at 60 °C to dry for 50–60 min, and store it in a sealed condition.

2.2 Preparation of Pristine GO and CGO Membranes

Pipette quantitative volumes from 0.1 mg/mL GO and carboxylated CGO standard solutions to prepare GO and CGO membranes with different loadings of 3, 6, 16, 31, and 47 $mg \cdot m^{-2}$.

2.3 Preparation of Intercalation-Modified Membranes

Prepare mixed solutions with GO/CGO to Ca^{2+} concentration ratios of 1:15, 1:20, and 1:30, respectively. After sonication for 30 min, form membranes by vacuum filtration, and then dry in a vacuum oven at 50 °C for 12 h. Similarly, prepare mixed solutions with GO/CGO to EDA concentration ratios of 1:2, 1:5, and 1:10. After sonication for 30 min, form membranes by vacuum filtration, and dry the wet membranes at 50 °C for 11 h.

3. Investigation of GO and CGO performance

3.1 Optimization of GO and CGO Loading Amount

Under cross-flow filtration conditions, the pure water flux, NaCl rejection, and $MgSO_4$ rejection of GO/CGO membranes with different loading amounts were tested to evaluate their water treatment performance.

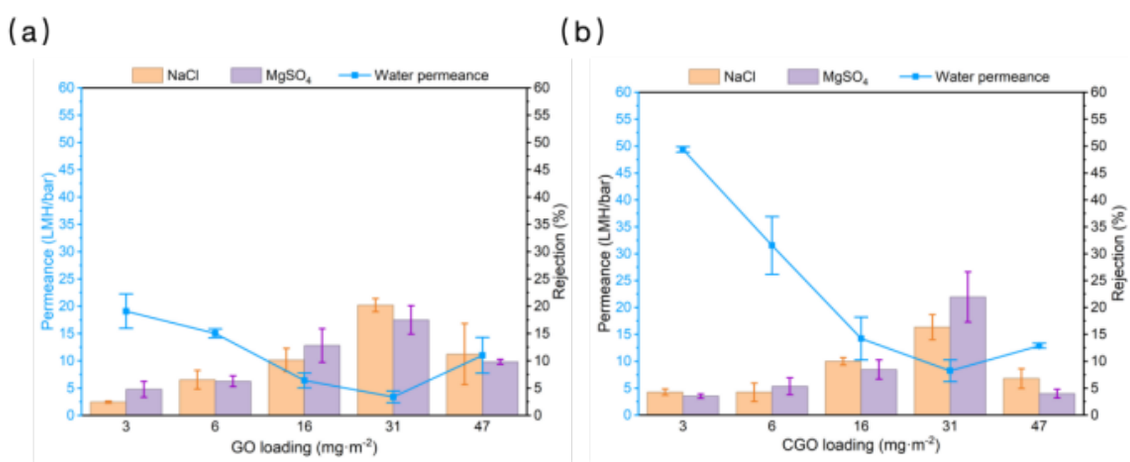

Figure 2. Water flux , NaCl and $MgSO_4$ rejection of membranes at different loadings: (a) GO membranes; (b) CGO membranes

As shown in Figure 2, with the gradual increase of GO loading from 3 $mg \cdot m^{-2}$ to 31 $mg \cdot m^{-2}$, the rejection rates of NaCl and $MgSO_4$ increased continuously, while the water flux declined gradually. This can be attributed to the progressive stacking of GO nanosheets on the substrate surface, which increased the membrane thickness and progressively narrowed the interlayer nanochannels, thereby enhancing the ion sieving effect while simultaneously increasing the resistance to water transport[7]. At a loading of 31 $mg \cdot m^{-2}$, the membrane achieved a favorable balance between permeability and rejection per-

formance. By comparison, the CGO membrane exhibited a similar trend over the same loading range, yet its overall water flux was notably higher than that of the GO membrane. This is mainly because more carboxyl groups were introduced on the CGO surface, which on the one hand enhanced the membrane hydrophilicity, and on the other hand, the electrostatic repulsion between carboxyl groups could, to a certain extent, suppress the tight stacking of nanosheets and make the membrane structure more uniform, thus maintaining a certain rejection capability while improving the flux. [8] When the loading was further increased to 47 $mg \cdot m^{-2}$, both GO and CGO membranes exhibited a decrease in rejection and an increase in flux. This is likely due to the excessive membrane thickness, which makes the membrane prone to local structural loosening or even detachment under cross-flow filtration conditions, resulting in defect channels on the membrane surface and thereby deteriorating the separation performance[9]. Therefore, the optimal loading for both GO and CGO membranes was determined to be 31 $mg \cdot m^{-2}$.

3.2 Analysis of Inorganic Salt Rejection Performance

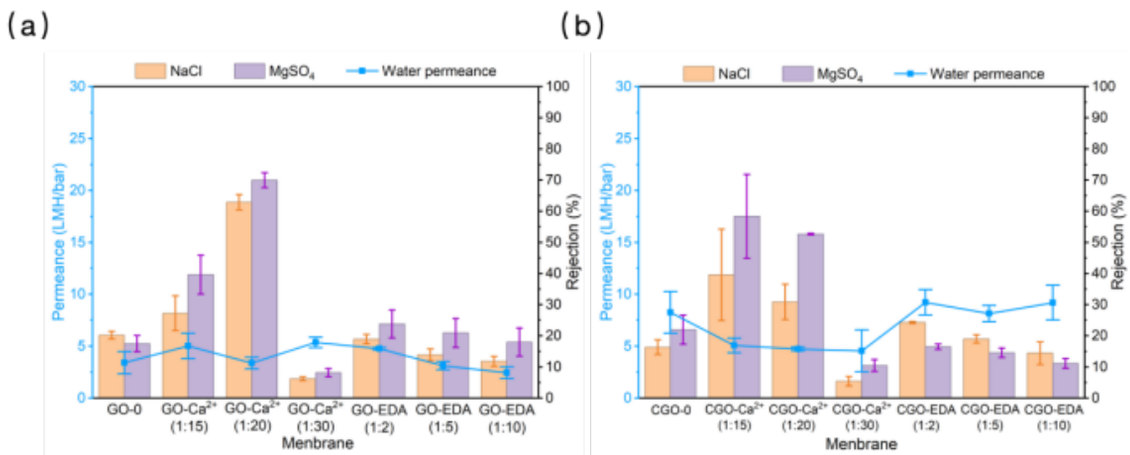

Figure 3. Water flux , NaCl and $MgSO_4$ rejection of intercalated GO/CGO membranes with different mass ratios: (a) GO-intercalated membranes; (b) CGO-intercalated membranes

After the optimal loading was determined, the GO and CGO solutions at the optimal loading were mixed with Ca^{2+} and EDA for intercalation, and the effect of intercalation at different mass ratios on inorganic salt rejection was investigated. As shown in Figure 3, the intercalation method and mass ratio significantly affected the inorganic salt rejection performance of the membranes. In the Ca^{2+} intercalation system, as the mass ratio increased from 1:15 to 1:20, the rejection of both salts improved markedly, indicating that an appropriate amount of Ca^{2+} made the interlayer structure denser through coordination, which was beneficial for ion sieving; however, when the ratio was further increased to 1:30, the rejection decreased instead. This is mainly because excessive Ca^{2+} resulted in a non-uniform membrane layer structure and the formation of locally larger channels, thereby reducing separation performance. Moreover, due to the non-uniform stacking of nanosheets, uneven stress distribution tends to occur inside the membrane during actual filtration, which can further cause surface structural anomalies. Under high-ratio Ca^{2+} intercalation conditions, although the interlayer spacing may be expanded in localized regions, the overall structural stability decreases, leading to membrane performance degradation.

4. Conclusions

In addressing the structural regulation and separation performance issues of GO and CGO membranes in water treatment, this study systematically investigated the relationship between membrane structural changes and separation performance by adjusting the loading amount and introducing Ca^{2+} and EDA for intercalation modification. The main conclusions are as follows:First, as the GO/CGO loading increased, the rejection rate of the membranes gradually improved while the water flux decreased. At a loading of 31 $mg \cdot m^{-2}$, the membranes achieved a favorable balance between permeability and rejection. Compared with GO membranes, CGO membranes exhibited better hydrophilicity and higher water flux due to the introduction of carboxyl groups, along with a more uniform structure.Second, the inorganic salt rejection results demonstrated that Ca^{2+} intercalation at a ratio of 1:20 could significantly enhance rejection performance, whereas excessive addition caused performance degradation due to structural non-uniformity. EDA intercalation, on the other hand, generally reduced rejection capability but was beneficial for flux enhancement. In addition, the rejection of $MgSO_4$ by all membranes was higher than that of NaCl, reflecting a charge sieving effect.Overall, Ca^{2+} intercalation mainly improved rejection performance by making the membrane structure denser, while EDA intercalation enhanced water permeation by enlarging the interlayer

channels. These two methods play distinct roles in regulating the membrane structure.

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